Water soluble copolymers: 38. Synthesis and characterization of electrolyte responsive terpolymers of acrylamide, *N*-(4-butyl)phenylacrylamide, and sodium acrylate, sodium-2-acrylamido-2-methylpropanesulphonate or sodium-3-acrylamido-3-methylbutanoate

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Responsive associative terpolymers of acrylamide, 0.5 mol% *N*-(4-butyl)phenylacrylamide and 5 and 25 mol% of one of the following: sodium acrylate, sodium-2-acrylamido-2-methylpropanesulphonate or sodium-3-acrylamido-3-methylbutanoate were synthesized by a micellar polymerization method. Terpolymer composition was determined by a combination of u.v. spectroscopy and elemental analysis. Solution properties were determined by low shear rheometry as functions of polymer concentration, solution ionic strength, pH and urea concentration. The carboxylate terpolymers exhibited high viscosities in the presence of up to 0.5 M NaCl and 0.17 M $CaCl_2$, but lose much of their viscosity at low pH and high urea content. The sulphonate-containing terpolymers are less responsive at low pH and high electrolyte concentration than the carboxylate-containing terpolymers.

(Keywords: copolymers; terpolymers; polymerization)

INTRODUCTION

Hydrophobically associating, water soluble polymers are important in a number of areas including enhanced oil recovery, drag reduction, and for formulation in coatings and personal care items[1-6]. Intermolecular associations of the hydrophobic groups in aqueous solution result in network formation and a rapid increase in solution viscosity. Typically, $<2\%$ incorporation of the hydrophobic monomer into the polymer backbone is necessary to obtain associative behaviour. This concentration is below the detection limit of standard techniques such as n.m.r. or elemental analysis. Valint *et al.*[7-9] have overcome this difficulty by synthesizing *N*-aryl substituted acrylamides easily detected by u.v. spectroscopy, including *N*-(4-butyl)phenylacrylamide (BPAM) utilized as a termonomer in this paper.

Research in our laboratory has concentrated on tailored copolymers to gain a fundamental understanding of hydrophobic associations and to develop structure–property relationships[10-14]. In this work the synthesis and solution properties are reported of electrolyte-responsive terpolymers of acrylamide (AM) with BPAM and one of the following ionic monomers: sodium acrylate (NaA), sodium-2-acrylamido-2-methylpropanesulphonate (NaAMPS) or sodium-3-acrylamido-3-methylbutanoate (NaAMB) (*Figure 1*). Comparisons may be made between the sulphonate group (NaAMPS) and the carboxylate moiety (NaAMB and NaA). In addition comparisons may be made between two carboxylate monomers differing by a spacer group that effectively decouples the charged group from the polymer backbone. Previously we reported structure–property relationships for similar terpolymers with the non-chromophore containing *N*-decylacrylamide monomer[13-15]. Hydrophobic group incorporation into a polyelectrolyte allowed the interaction of hydrophobic attractions and electrostatic charge–charge repulsions to be investigated.

In this paper electrostatic and hydrophobic interactions, both intra- and intermolecular, are examined as functions of ionic strength, polymer structure and polymer concentration. Importantly, precise compositions of the hydrophobic monomer can be determined in each study.

EXPERIMENTAL

Materials and monomer synthesis

All chemicals were obtained from Aldrich Chemical Company. Reagent grade solvents were used without further purification. AM was recrystallized twice from

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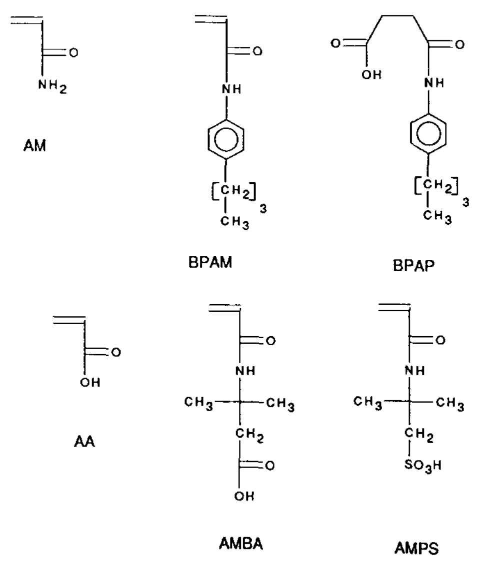

Figure 1 Monomers used in polymer synthesis and BPAM model compound

acetone, dried under vacuum and stored in a desiccator (m.p. 81–84°C). Acrylic acid (AA) was purified by vacuum distillation in the presence of copper sulphate to remove inhibitor prior to use. 2-Acrylamido-2-methylpropanesulphonic acid (AMPS) was obtained from Fluka Chemical Co. and recrystallized twice from a mixture of methanol and 2-propanol.

3-Acrylamido-3-methylbutanoic acid (AMBA) was synthesized via a Ritter reaction using acrylonitrile and 3,3-dimethylacrylic acid in the presence of water and excess sulphuric acid. The procedure of Hoke and Robbins[16] was employed for the synthesis of AMBA.

BPAM was synthesized from the reaction of 4-butylaniline with acryloyl chloride with triethylamine as the acid receptor using the method described by Valint *et al.*[7]. 4-Butylaniline was recovered as a clear liquid after vacuum distillation at 100°C/6–9 mm Hg. The crude product (90% yield) was recrystallized from a mixture of acetone and cyclohexane at −5°C and a white product recovered (m.p. 101–102°C). Analysis: *FT*i.r. (KBr): N–H, 3290, C=C–H 3120, aliphatic CH_2, CH_3 2930 and 2860, C=O 1650, disubstituted aromatic 810 and 730 cm^{-1}. ^{13}C n.m.r. ($CDCl_3$): δ 13.6 (CH_3), 22.0 (CH_3–$\underline{CH_2}$), 33.3 (CH_3–CH_2–$\underline{CH_2}$–), 34.8 (benzyl–CH_2), 120.1, 126.9, 135.2, 139.0 (aromatic CH), 128.5 (=CH), 131.2 (CH_2=), 163.0 (C=O).

The model compound *N*-(4-butyl)phenylamidopropionic acid (BPAP) (*Figure 1*) was synthesized in a one-step reaction of 4-butylaniline with succinic anhydride as follows. Distilled 4-butylaniline (0.01 mol) was dissolved in dichloromethane (75 ml) in a 250 ml flask equipped with a mechanical stirrer, thermometer and addition funnel sealed with a drying tube. Succinic anhydride (0.01 mol) was dissolved in dichloromethane (100 ml) and added to the reaction mixture over 1 h at room temperature. A white precipitate formed and was filtered. The product was recrystallized from a mixture of acetone and hexane at −5°C resulting in white crystals (m.p. 154–156°C).

Polymer synthesis

A micellar polymerization technique[4] was used to prepare terpolymers with monomer feeds of 0.5 mol% BPAM and 5 and 25 mol% AA, AMBA or AMPS. The remaining polymer was composed of AM. An ionic surfactant, sodium dodecyl sulphate (SDS) in this study, is necessary to dissolve BPAM in the aqueous solution.

Each reaction was conducted in a 500 ml, three-necked, round-bottomed flask equipped with mechanical stirrer, nitrogen inlet and condenser. The appropriate amount of ionizable monomer was placed in 240 ml deionized water and the pH adjusted to 9 with NaOH to form the water soluble sodium salt (NaA, NaAMB or NaAMPS). SDS surfactant (7.93 g; 2.8×10^{-2} mol) and BPAM hydrophobic monomer (0.1117 g, 5.5×10^{-4} mol) were then added, respectively, and stirred under N_2 until a clear solution was observed. The AM monomer was then dissolved in this solution and heated to 50°C with stirring. Potassium persulphate (0.010 g, 3.7×10^{-5} mol) dissolved in deionized water (10 ml) was added for a total water volume of 250 ml and a total monomer concentration of 0.44 M. The polymerizations were conducted for 4–6 h followed by dilution of the polymer mixtures with equal amounts of water and precipitation into acetone. The polymers were washed extensively in acetone and then dried under vacuum for 24 h.

Polymer characterization

Polymer purification. After precipitation, the polymers were dried and redissolved in deionized water. The samples were then dialysed against deionized water through SpectraPor no. 4 dialysis tubing with a molecular weight cut off of 12 000–14 000 for a minimum of 7 days. The purified samples were then lyophilized to a constant weight. Attempts to determine molecular weights by light scattering were unsuccessful due to the associative nature of the terpolymers. Homopolyacrylamide prepared under identical conditions had a molecular weight of 1.0×10^6–1.5×10^6. Since all polymer series were prepared under identical conditions, comparisons of solution behaviour should be qualitatively valid.

Elemental analysis. Elemental analyses for carbon, hydrogen and nitrogen of the terpolymers were conducted by M-W-H Laboratories of Phoenix, AZ, USA. In addition, sulphur analysis of representative samples of polymers (not containing a sulphur based monomer) was performed to confirm the absence of residual surfactant.

U.v. analysis. U.v. spectroscopy was used in determining polymer composition of those polymers containing monomers with chromophoric groups. All spectra were obtained with a Perkin-Elmer Lambda 6 spectrometer. Beer–Lambert plots were obtained at 250 nm for the water soluble sodium salt of the model compound and compared with polymer absorbance. Polyacrylamide was used as a reference to remove any background absorbance.

Solution rheology. Stock solutions were prepared by dissolving the appropriate amount of salt in deionized water. Lypholized polymer was weighed into a glass container and solvent added. Typical polymer concentrations were 0.2 g dl^{-1}. The polymers were dissolved by gentle shaking on an orbital shaker for 14 days to allow complete hydration before further dilutions of these stock solutions were made. Viscosity experiments were conducted on a thermostatically controlled Contraves LS 30 low shear rheometer.

Compositional calculations. Polymer compositions were determined using a combination of u.v. spectroscopy and elemental analysis. The concentration of BPAM was determined directly from a Beer–Lambert plot (in $\mathrm{mol\,l^{-1}}$). For terpolymers, three variables and two equations were used where variable C represents the moles of BPAM in 100 g of polymer determined from u.v., A the moles of ionic monomer in 100 g of polymer and B the moles of AM in 100 g of polymer as determined from matrix algebra. The coefficients are the number of carbons and nitrogens in each monomer. After determining A and B (with C known from u.v.) for each polymer sample, mole per cent compositional data were calculated to determine the relative abundance of each of the monomers. Equations (1)–(5) were used for BPAM/NaAMPS where A is NaAMPS and B is AM.

$$\%\mathrm{C}/12.01 = 7A + 3B + 13C \tag{1}$$

$$\%\mathrm{N}/14.01 = 1A + 1B + 1C \tag{2}$$

$$\mathrm{Mol\%\ NaAMPS} = 100A/(A + B + C) \tag{3}$$

$$\mathrm{Mol\%\ AM} = 100B/(A + B + C) \tag{4}$$

$$\mathrm{Mol\%\ BPAM} = 100C/(A + B + C) \tag{5}$$

Similar equations [(6)–(10)] were used to determine terpolymer compositions for the BPAM/NaAMB series where A, B and C are NaAMB, AM and BPAM, respectively.

$$\%\mathrm{C}/12.01 = 8A + 3B + 13C \tag{6}$$

$$\%\mathrm{N}/14.01 = 1A + 1B + 1C \tag{7}$$

$$\mathrm{Mol\%\ NaAMB} = 100\mathrm{A}/(\mathrm{A} + B + C) \tag{8}$$

$$\mathrm{Mol\%\ AM} = 100B/(A + B + C) \tag{9}$$

$$\mathrm{Mol\%\ BPAM} = 100C/(A + B + C) \tag{10}$$

Equations (11)–(15) were used to determine terpolymer compositions for the BPAM/NaA series. A, B and C represent monomers NaA, AM and BPAM, respectively.

$$\%\mathrm{C}/12.01 = 3A + 3B + 13C \tag{11}$$

$$\%\mathrm{N}/14.01 = 0A + 1B + 1C \tag{12}$$

$$\mathrm{Mol\%\ NaA} = 100A/(A + B + C) \tag{13}$$

$$\mathrm{Mol\%\ AM} = 100B/(A + B + C) \tag{14}$$

$$\mathrm{Mol\%\ BPAM} = 100C/(A + B + C) \tag{15}$$

RESULTS AND DISCUSSION

Previous work in our laboratory has led to successful preparation of hydrophobically modified polyelectrolyte terpolymers with pH- and salt-responsive viscometric behaviour[15]. However, we were concerned by the inability to absolutely quantify the decylacrylamide content. The introduction of the phenyl moiety into the hydrophobic monomer reported by Valint *et al.*[7] allowed us to substitute BPAM for decylacrylamide. The resulting terpolymers had similar properties to those prepared previously[15], but importantly, compositions could be successfully determined by a combination of elemental analysis and u.v. spectroscopy. Terpolymers containing 5 and 25 mol% ionic monomer in the feed were prepared to represent low charge density and high charge density polymers, respectively. The hydrophobic group was incorporated into the polymer at ~0.5 mol% via the micellar polymerization with remaining backbone composed of AM. Monomer structures are shown in *Figure 1.*

Ionic strength of the terpolymer solutions was varied from 0.01 to 0.5 to evaluate the effects on polymer rheology. The effects of the divalent cation $\mathrm{Ca^{2+}}$ (0.17 M $\mathrm{CaCl_2}$ or an ionic strength of 0.5) and the effects of urea in water were also evaluated.

Compositional analysis

Compositional data (*Table 1*) indicate agreement between the feed ratios and copolymer composition for the AM and ionic comonomer, but hydrophobic monomer incorporation decreases as much as 50% with increasing ionic group incorporation. Analogous non-ionic copolymers were reported to result in BPAM monomer incorporation >85% of the feed ratio[7,14]; therefore, the introduction of charged groups into the backbone must interfere with hydrophobic group incorporation. The growing polymer chain bearing anionic charge groups is less likely to interact with the anionically charged surface of the micelle in which the hydrophobic monomer is solubilized. This also implies that the hydrophobic monomers are less likely to have charged groups as nearest neighbours. Parallel studies in our research group support a somewhat blocky incorporation of hydrophobic monomers at low surfactant/monomer ratios[17].

Solution properties of BPAM terpolymers

Effect of ionic strength. Three-dimensional plots can be used to show topological relationships among

Table 1 BPAM terpolymer compositional data from u.v. and elemental analysis

Sample no.	M1:M2:M3[a]	%C	%N	U.v.[b] ($\times 10^3$)	AM (mol%)	NaAMB (mol%)	BPAM[c] (mol%)
BPAM/NaAMB-5	95:5:0.5	47.51	16.54	5.32	93.4	6.2	0.45
BPAM/NaAMB-25	72:25:0.5	49.39	12.86	3.41	70.8	28.9	0.37
						NaAMPS	
BPAM/NaAMPS-5	95:5:0.5	46.46	46.16	5.26	91.8	7.7	0.46
BPAM/NaAMPS-25	75:25:0.5	40.45	11.59	2.09	73.5	26.2	0.25
						NaA	
BPAM/NaA-5	95:5:0.5	44.18	15.42	5.47	90.7	10.5	0.45
BPAM/NaA-25	95:25:0.5	41.80	11.76	2.99	72.7	27.1	0.26

[a] M1, acrylamide; M2, ionic group NaAMB, NaAMPS, NaA; M3, BPAM feed compositions
[b] U.v. absorbance scanned at 250 nm
[c] From u.v. determination

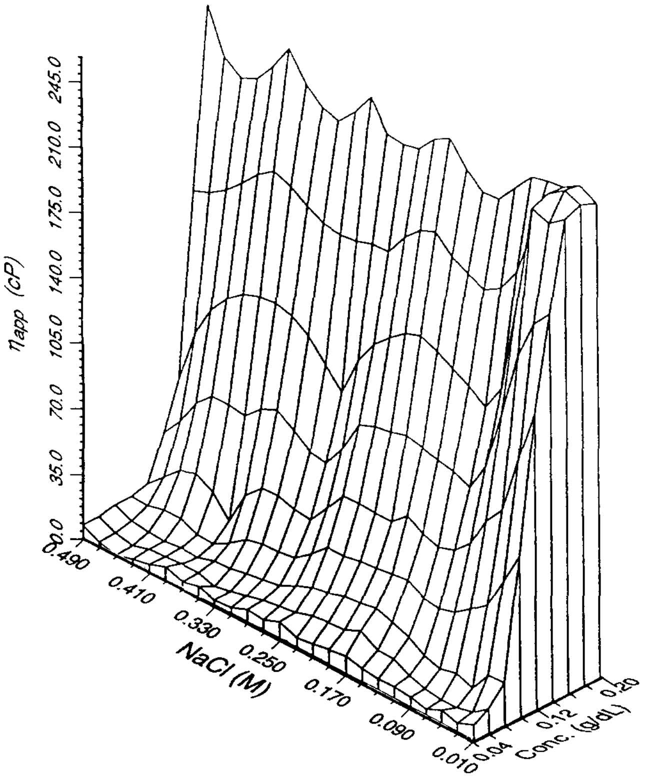

Figure 2 η_{app} as a function of polymer concentration and solution ionic strength for the BPAM/NaAMPS-5 terpolymer

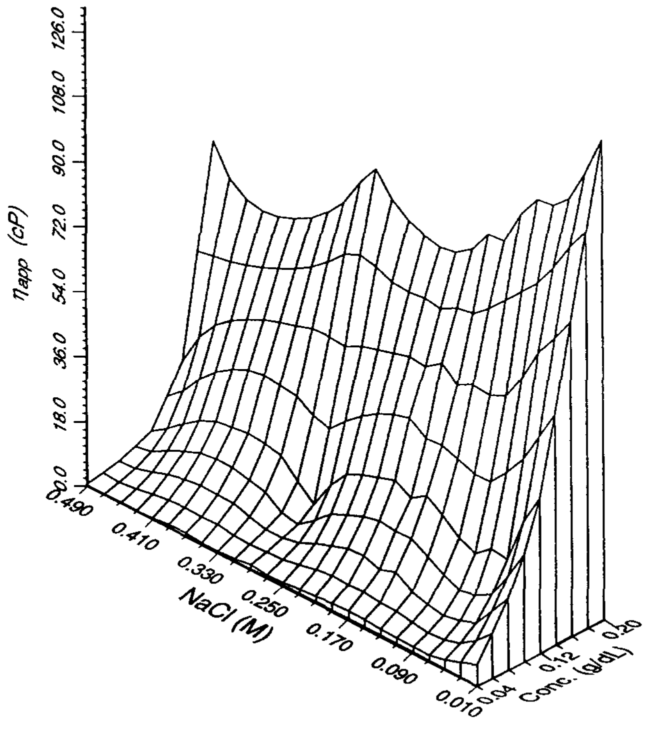

Figure 3 η_{app} as a function of polymer concentration and solution ionic strength for the BPAM/NaAMPS-25 terpolymer

apparent viscosity, terpolymer concentrations and ionic strength. Polymer concentration varies from 0.04 to 0.20 g dl^{-1} and the NaCl concentrations are 0.01, 0.05, 0.10 and 0.50 M. When gels with viscosities greater than the upper range of the Contraves (operating at 25°C and a shear rate of 6 s^{-1}) were formed, an upper limit of 250 cP is placed on the graphs.

The BPAM/NaAMPS-5 polymer has a high viscosity at low ionic strength typical of polyelectrolytes. However unlike traditional polyelectrolytes which exhibit loss of hydrodynamic volume with added electrolyte, this terpolymer above the overlap concentration (C^*) maintains viscosity due to intermolecular hydrophobic associations (*Figure 2*). Gel formation occurs at concentrations of >0.16 g dl^{-1} at all ionic strengths investigated.

The BPAM/NaAMPS-25 polymer has higher apparent viscosity than the low charge density analogues at concentrations below C^*. Above C^*, however, the low charge density polymers have higher viscosities (*Figure 3*).

The BPAM/NaAMB-5 polymer has behaviour similar to that of the BPAM/NaAMPS-5 terpolymer. Viscosity is maintained with increasing ionic strength above C^* (*Figure 4*). The BPAM/NaAMB-25 terpolymer behaves like a typical polyelectrolyte (*Figure 5*), while the BPAM/NaA-5 terpolymer behaves in a fashion similar to the other low charge density polymers (*Figure 6*). The BPAM/NaA-25 (*Figure 7*) also has a higher apparent viscosity at low polymer concentration and lower viscosity above C^* than low charge density analogues.

The low charge density terpolymers have lower viscosities below C^* and higher viscosities above C^* than the high charge density systems. Below C^* the ionic forces determine the solution behaviour, but above C^* the hydrophobic interactions dominate the solution rheology. Below C^*, the increase in charge density from 5 to 25 mol% results in polymers with larger hydrodynamic volumes. Above C^*, where viscosity enhancement is due to interpolymer associations, the low charge density, charge–charge repulsions act to expand the polymer coil and to enhance water solubility; however, these are not sufficient to disrupt hydrophobic interactions. Higher

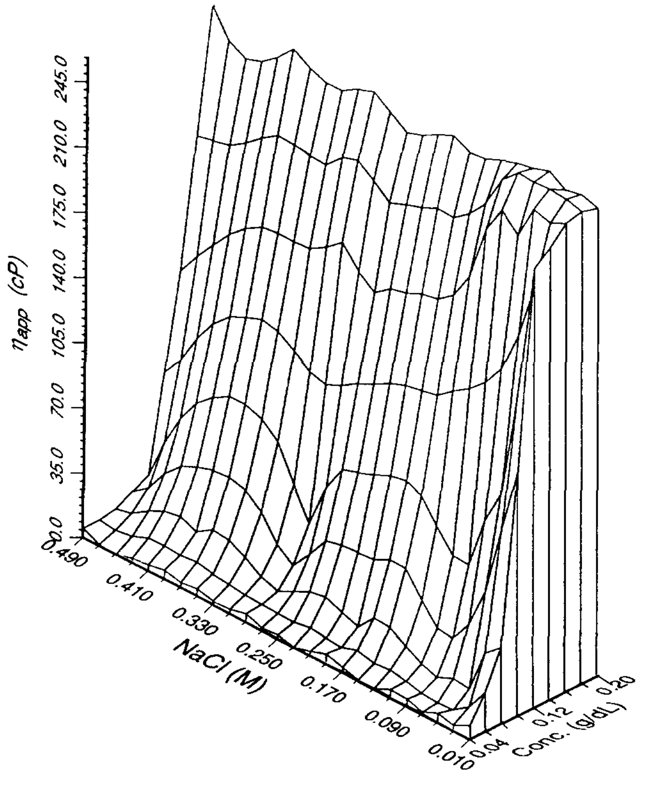

Figure 4 η_{app} as a function of polymer concentration and solution ionic strength for the BPAM/NaAMB-5 terpolymer

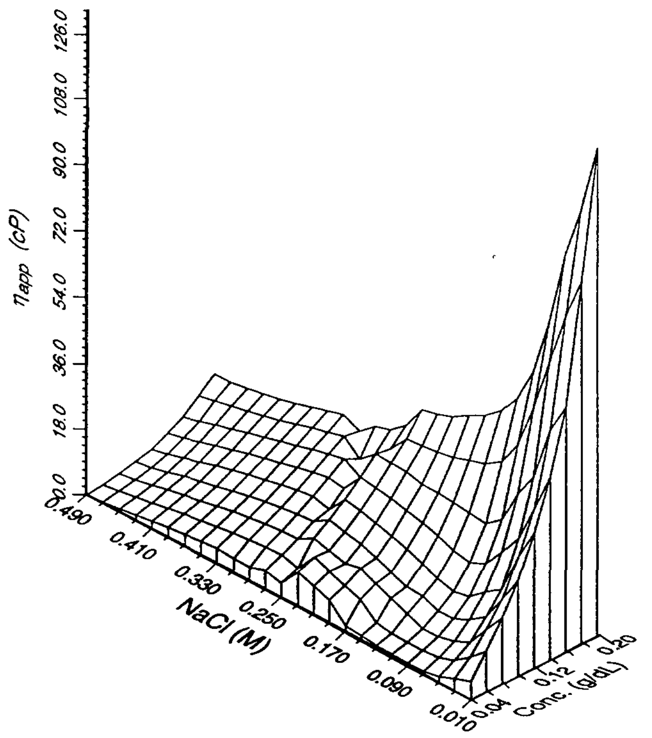

Figure 5 η_{app} as a function of polymer concentration and solution ionic strength for the BPAM/NaAMB-25 terpolymer

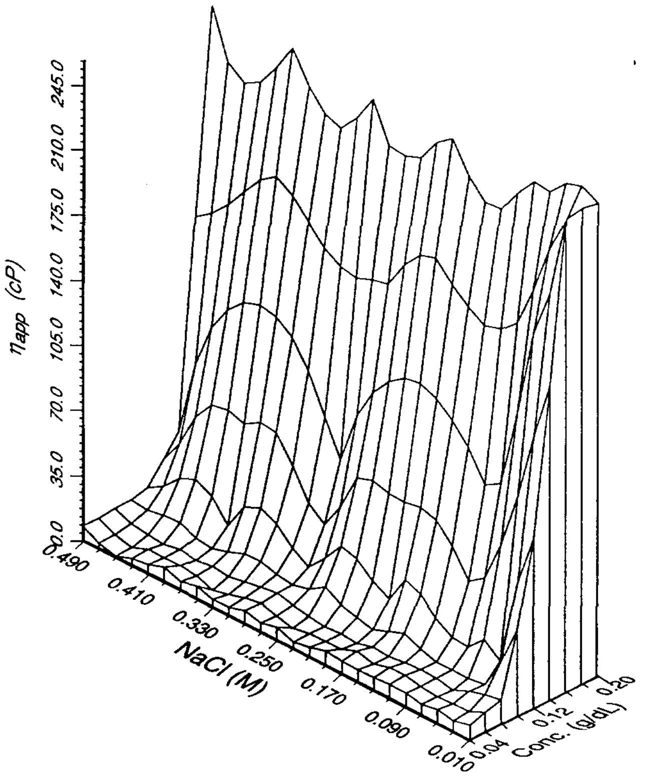

Figure 6 η_{app} as a function of polymer concentration and solution ionic strength for the BPAM/NaA-5 terpolymer

charge densities both reduce the amount of hydrophobic group incorporated during polymerization and disrupt hydrophobic interactions.

The BPAM/NaAMPS-25 terpolymer (*Figure 3*) contains one-third less hydrophobic monomer than the BPAM/NaAMB-25 polymer (*Figure 5*), yet has a much higher viscosity at higher salt concentrations. This indicates that the polyelectrolyte and hydrophobic interactions are acting in concert and that microstructural placement of the hydrophobic groups is as important as the hydrophobic monomer concentration. The soft NaAMPS anions are less affected by solvent ionic strength and therefore retain a higher viscosity in salt solutions. The NaAMB carboxy anion repulsions are effectively shielded by the counterions (site binding) resulting in a loss of hydrodynamic volume. The BPAM/NaA terpolymers (*Figures 6* and *7*) maintain high viscosity at all ionic strengths. The proximity of the charged group to the backbone may result in less hydrophobic disruption, although some reduction in viscosity above C^* is also evidenced by increasing charge density in these systems.

Viscosity plots also illustrate that the high charge density NaAMPS and NaAMB polymers possess high viscosities at low concentration; however, the low charge density polymers associate efficiently at concentrations between 0.08 g dl^{-1} and 0.12 g dl^{-1} resulting in a rapid rise in the apparent viscosity *versus* concentration plot. The NaA containing polymers are qualitatively different in that high charge density systems maintain higher viscosity up to a limiting ionic strength.

The effect of calcium salt addition is demonstrated for the BPAM/NaAMPS-5 (*Figure 8*) and BPAM/NaAMB-5 (*Figure 9*) solutions. As might be expected, the Ca^{2+} ion causes greater reduction in hydrodynamic volume than the Na^+ ion. Although phase separation often occurs in some polyelectrolyte systems, these low charge density copolymers retain solubility and high reduced viscosities up to concentrations of 0.2 g dl^{-1}. At higher terpolymer concentrations gelation occurs.

Effect of urea. Reduced viscosity was evaluated as a function of added urea, reported to be a disrupter

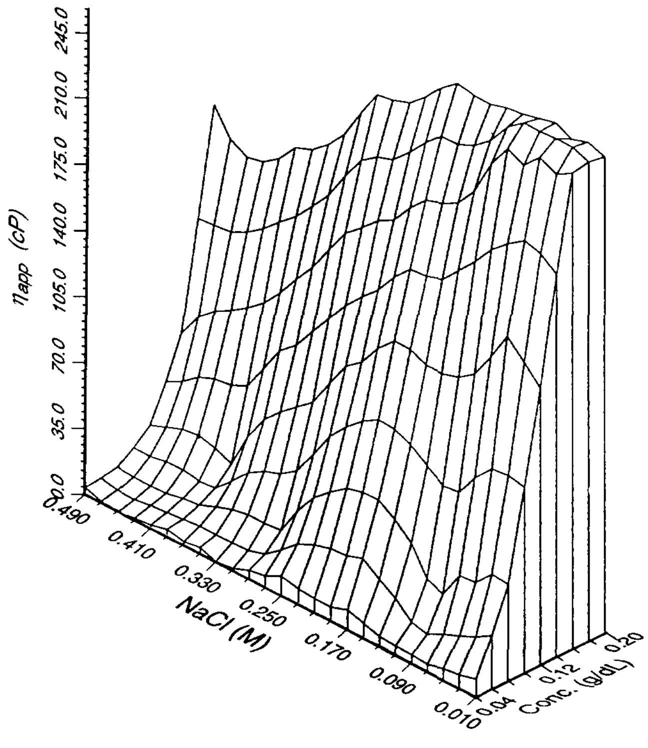

Figure 7 η_{app} as a function of polymer concentration and solution ionic strength for the BPAM/NaA-25 terpolymer

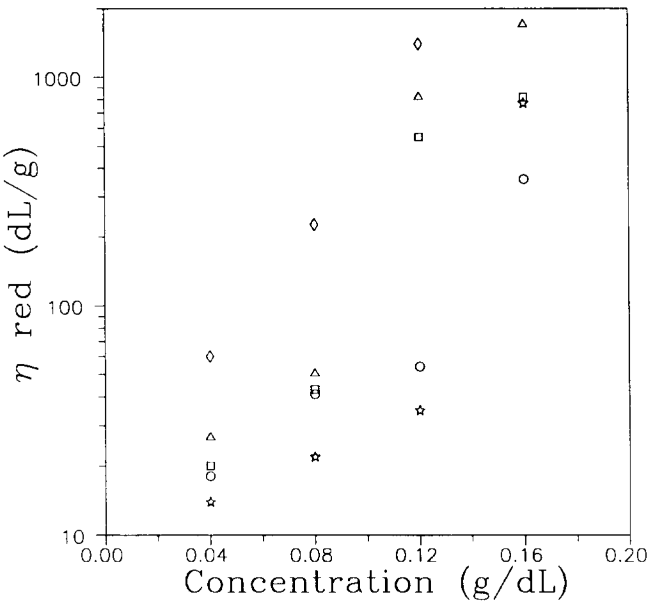

Figure 8 η_{red} *versus* polymer concentration for the BPAM/NaAMPS-5 terpolymer in NaCl and $CaCl_2$: (○) 0.5 M NaCl; (□) 0.1 M NaCl; (△) 0.05 M NaCl; (◇) 0.01 M NaCl; (☆) 0.17 M $CaCl_2$

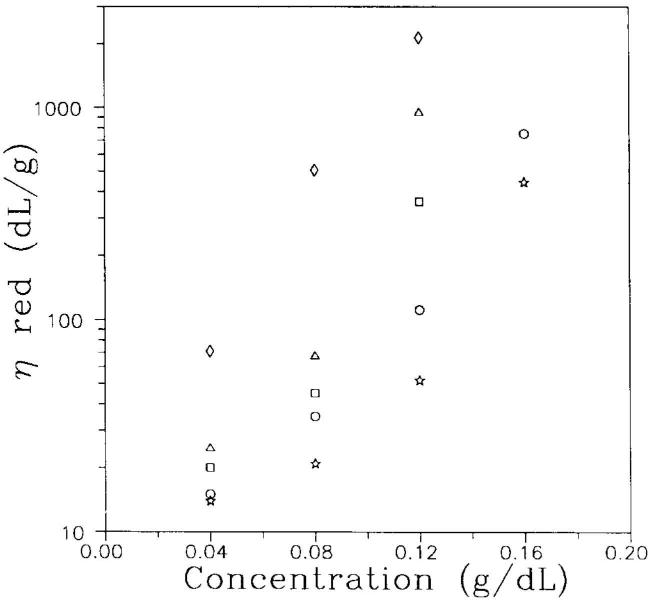

Figure 9 η_{red} *versus* polymer concentration for the BPAM/NaAMB-5 terpolymer in NaCl and $CaCl_2$. Symbols as in *Figure 8*

of hydrophobic interactions. Reduced viscosity was measured at 0.5 (*Figure 10*) and 0.01 M NaCl (*Figure 11*) in 0, 1, 3, 5 and 7 M urea at a polymer concentration of 0.1 g dl^{-1}. The low charge density polymers BPAM/NaAMPS-5, BPAM/NaAMB-5 and BPAM/NaA-5 were selected because they appear to have the most numerous hydrophobic associations. A 10-fold decrease in reduced viscosity was observed while increasing urea concentration from 0 to 7 M urea at low ionic strength for the BPAM/NaAMB system; the least drop in viscosity was observed for the BPAM/NaA polymers. In 0.5 M NaCl, the viscosity decrease is much less pronounced for BPAM/NaAMB (55 to 30 dl g^{-1}) with increasing urea concentration (0 to 3 M). At both ionic strengths in 7 M urea, the viscosities of the terpolymers decrease to approximately the value of their analogous, unmodified copolymers. The urea clearly disrupts the hydrophobic interactions, resulting in deaggregation of the polymer network. The large apparent molecular weight resulting from the interaction of several polymer chains decreases to that of the unmodified coil in solution.

CONCLUSIONS

Terpolymers of BPAM, AM, and anionic monomers, NaA, NaAMPS and NaAMB were prepared by a micellar polymerization method and were characterized utilizing elemental analysis and u.v. spectroscopy. U.v. comparisons of model compound BPAP with the

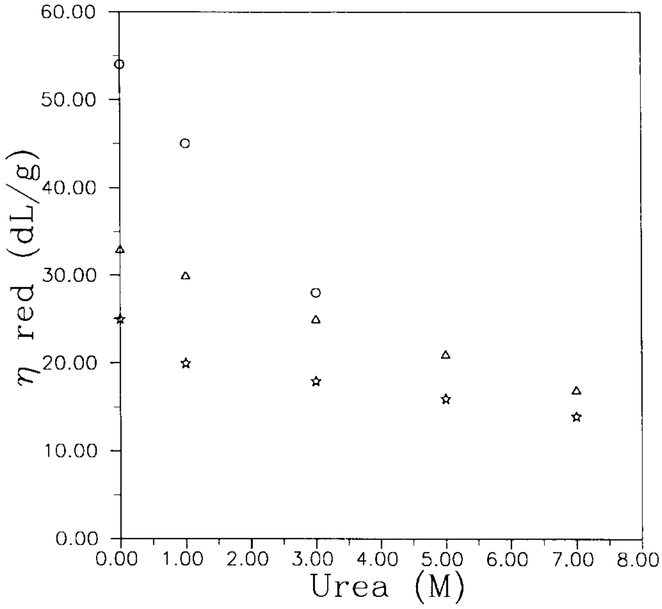

Figure 10 η_{red} *versus* urea concentration for the low charge density BPAM terpolymers in 0.5 M NaCl: (○) BPAM/NaAMB-5; (△) BPAM/ NaAMPS-5; (☆) BPAM/NaA-5

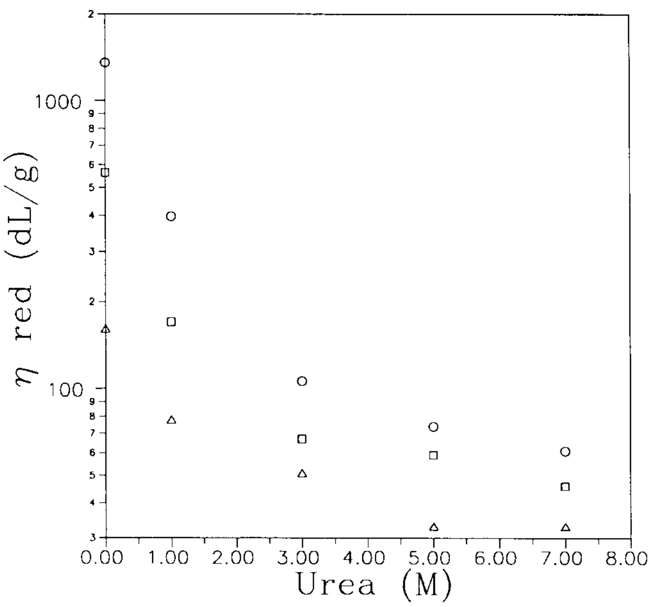

Figure 11 η_{red} *versus* urea concentration for the low charge density BPAM terpolymers in 0.01 M NaCl: (○) BPAM/NaAMB-5; (□) BPAM/NaAMPS-5; (△) BPAM/NaA-5

terpolymers allowed direct analysis of hydrophobe content.

The low charge density polymers exhibit lower viscosities below C^* and higher viscosities above C^* than their high charge density analogues. All of the low charge density polymers form gels at concentrations above $0.20\,\mathrm{g\,dl^{-1}}$. Below C^*, the electrostatic repulsions dominate solution behaviour and the polymers with the most ionic monomer content have larger hydrodynamic volumes. Above C^* interpolymer aggregation and network formation is responsible for the large apparent viscosities. The low charge density polymers have the higher viscosities above C^* due to less electrostatic interference of hydrophobic association.

The order of the high charge density systems with the most efficient association and, therefore, highest viscosities at a given concentration and ionic strength is BPAM/NaA > BPAM/NaAMPS > BPAM/NaAMB. The presence of ionic groups adjacent to hydrophobic groups may result in a disruption of the hydrophobic effect through water restructuring. If runs of AM separate the ionic groups from the hydrophobic blocks, synergistic effects may be observed where the electrostatic repulsions can result in chain expansion and the hydrophobic groups may also maintain interpolymer associations. In this instance the NaAMPS terpolymers are less shielded by counterions and maintain larger hydrodynamic volumes than NaAMB terpolymers which collapse with increasing ionic strength.

Reduced viscosity decreases measurably with increasing urea content. Urea interferes with hydrophobic interactions and reduces the intermolecular associations. In 7 M urea the associative polymers approach viscosities similar to those of unmodified analogues.

The difficulty of determining precise molecular weights due to polymer associations in dilute solution continues to be a major obstacle. Additionally the mechanism of the micellar polymerization and evidence for block hydrophobic runs at low hydrophobic monomer feed ratios are being investigated in our laboratory and will be reported in a subsequent paper.

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